

Problem Set 8 - 5.3b,c, 5.4, 5.10, 5.12, 5.19, 5.30

5.3b Looking at the table of Henry's Law constants on p. 194, we see that for methane in water $k_B = 39 \times 10^3 \text{ atm}$ at 25°C . Using Henry's Law, $P_B = k_B X_B$,

$$X_B = \frac{P_B}{k_B} = \frac{1 \text{ atm}}{39 \times 10^3 \text{ atm}} = 2.6 \times 10^{-5}$$

Since the solution is dilute, the total number of moles is approximately equal to the number of moles of water:

$$X_B = \frac{n_B}{n_B + n_{H_2O}} \approx \frac{n_B}{n_{H_2O}}$$

So to convert to molarity,

$$\left(\frac{n_B}{n_{H_2O}} \right) \left(\frac{n_{H_2O}}{\text{volume}} \right) \approx X_B \left(\frac{n_{H_2O}}{1L} \right) = \left(\frac{2.6 \times 10^{-5} \text{ mol}}{1 \text{ mol } H_2O} \right) \left(\frac{55.6 \text{ mol } H_2O}{1L} \right) = 1.4 \times 10^{-3} M$$

5.3c Think about a can of soda; the bubbles stay in solution (your drink stays "fizzy") longer when you have ice in it than when it is warm. Alternately, you could calculate this using a similar procedure as in part b, but using the Henry's law constant at 0°C

5.4 We are told that the reaction $Mb + O_2(aq) \rightarrow MbO_2$ occurs with $\Delta G^\circ = -30.0 \text{ kJ/mol}$ at 298 K and $pH = 7.0$. Furthermore, we are told that the pressure of air, $p_{O_2} = (30 \text{ torr}) \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 0.0395 \text{ atm}$. Then, as in 5.3b, we use the table of Henry's Law constants on p. 194 to figure out how much oxygen is in the solution:

$$X_B = \frac{P_B}{k_B} = \frac{0.0395 \text{ atm}}{43 \times 10^3 \text{ atm}} = 9.18 \times 10^{-7}$$

$$[O_2(aq)] = X_B \left(\frac{55.6 \text{ mol } H_2O}{1L} \right) = 5.10 \times 10^{-5} M$$

Having established this, we may now solve for the ratio of MbO_2/Mb as follows:

$$\Delta G^\circ = -RT \ln K$$

$$K = \text{Exp} [-\Delta G^\circ / RT] = \frac{[MbO_2]}{[Mb][O_2(aq)]}$$

$$\frac{[MbO_2]}{[Mb]} = [O_2(aq)] \text{Exp} [-\Delta G^\circ / RT]$$

$$\frac{[MbO_2]}{[Mb]} = \frac{5.10 \times 10^{-5} M}{1M} \text{Exp} [-(-30.0 \text{ kJ/mol}) / (8.315 \times 10^{-3} \text{ kJ/mol K})(298 \text{ K})] = 9.24$$

5.10a According to Henry's Law, we know that $X_B = p_B/k_B$. As in the previous problem, since the gas concentration is low, we can assume that the molar volume of the solution is that of water, i.e.,

$$[gas(aq)] \approx \left(\frac{p_{gas}}{k_{gas}} \right) \left(\frac{55.6 \text{ mol } H_2O}{1L} \right)$$

Tabulating the results for each of the gases, and using the Henry's Law constants from p. 194

	$p_{gas}(\text{atm})$	$k_{gas}(10^3 \text{ atm})$	$X_{gas}(10^{-6})$	$[gas(aq)](\text{mM})$
O_2	0.20	43	4.7	0.26
N_2	0.75	85	8.8	0.49
CO_2	0.05	1.61	31	1.7

5.10b According to Raoult's law, we know that $p_{solv} = p_{solv}^\bullet X_{solv}$, where for water, $p_{H_2O}^\bullet = 23.756$ torr. First we calculate

$$X_{H_2O} = 1 - \sum_{B \in \text{solutes}} X_B = 1 - (4.7 + 8.8 + 31) \times 10^{-6} = 0.9999555$$

Then by Raoult's law, $p_{H_2O} = p_{H_2O}^\bullet X_{H_2O} = (23.756 \text{ torr})(0.9999555) = 23.755$ torr.

5.12a Since the cell remains unchanged in 0.7 wt % $NaCl$, but swells/shrinks in other solutions, we conclude that the osmotic pressure of the cell cytoplasm is equal to that of a 0.7 wt % $NaCl$ solution, since osmotic pressure is a colligative property. From the freezing point depression $\Delta T = k_f m$, where ΔT is the change in freezing point, $k_f = 1.86^\circ\text{C/molal}$ is the freezing-point-depression constant for water, and m is the molality (of ions) of the solution, we can determine the molality (of ions) of the solution,

$$m = \frac{\Delta T}{k_f} = \frac{0.406^\circ\text{C}}{1.86^\circ\text{C/molal}} = 0.218 \text{ m}$$

To convert to molarity (of ions), we multiply by the density of water at 25°C

$$\frac{0.218 \text{ mol ions}}{1 \text{ kg } H_2O} \times \frac{1 \text{ kg } H_2O}{0.992 \text{ L}} = 0.220 \text{ M ions}$$

Then, to find the osmotic pressure, we simply use the equation

$$\Pi = cRT = (0.220 \text{ M ions})(0.08205 \text{ L atm/mol K})(298 \text{ K}) = 5.38 \text{ atm}$$

Note that we can also work out the osmotic pressure directly from the percent-weight information without using the freezing point depression, as follows:

$$\begin{aligned} \frac{0.7 \text{ g } NaCl}{100 \text{ g total}} &= \frac{0.7 \text{ g } NaCl}{99.3 \text{ g } H_2O} \\ \frac{0.7 \text{ g } NaCl}{99.3 \text{ g } H_2O} \times \frac{1 \text{ mol } NaCl}{58.5 \text{ g}} \times \frac{1000 \text{ g } H_2O}{0.992 \text{ L}} &= 0.121 \text{ M } NaCl \end{aligned}$$

However, in water, each $NaCl$ dissociates to form two ions, a Na^+ and a Cl^- , and since freezing point depression is a colligative property, what matters is the number of species in solution. So, our concentration of ions, which we need for calculation the osmotic pressure, or other colligative properties, is twice this amount

$$\Pi = cRT = (2 \times 0.121 \text{ mol/L})(0.08205 \text{ L atm/mol K})(298 \text{ K}) = 5.9 \text{ atm}$$

5.12b Since osmotic pressure is a colligative property, all that matters is the number of moles of our solution, i.e., we want to have the same molarity of sucrose as we had molarity of $NaCl$:

$$\frac{0.220 \text{ mol sucrose}}{1 \text{ L } H_2O} \times \frac{0.342 \text{ kg sucrose}}{1 \text{ mol sucrose}} = \frac{0.0752 \text{ kg sucrose}}{1 \text{ L } H_2O}$$

The mass of water is (using the density at 25°C given above),

$$(1 \text{ L } H_2O) \times \frac{1 \text{ kg}}{0.992 \text{ L}} = 1.008 \text{ kg } H_2O$$

So the total mass of the solution is

$$m_{total} = m_{sucrose} + m_{H_2O} = 0.0752 \text{ kg} + 1.008 \text{ kg} = 1.0834 \text{ kg}$$

and the percent weight of sucrose is

$$\% \text{ wt sucrose} = \frac{m_{sucrose}}{m_{total}} \times 100\% = \frac{0.0752 \text{ kg}}{1.0834 \text{ kg}} \times 100\% = 6.94\% \text{ wt}$$

You should be able to do this for yourself using the other molarity that we determined in part (a). Since sucrose does not dissociate, what you see is what you get (so to speak). However, a direct conversion between weight percent *NaCl* and weight percent *sucrose* will only be correct if you take into effect the extra factor of two in the number of ions in the *NaCl* solution.

5.19 The pressure at 300 meters is simply given by,

$$p = \rho gh = (993.3328 \text{ kg/m}^3)(9.8 \text{ m/s}^2)(300 \text{ m}) = 2.92 \times 10^6 \text{ kg/m} \cdot \text{s}^2 = 2.92 \times 10^6 \text{ Pa}$$

where ρ is the density of seawater at 37°C (assuming it is constant), g is the acceleration due to gravity, and h is the depth. To convert to atmospheres,

$$(2.92 \times 10^6 \text{ Pa}) \times \left(\frac{1 \text{ atm}}{1.013 \times 10^5 \text{ Pa}} \right) = 28.8 \text{ atm}$$

However, this is only the pressure due to the water. We also have the 1 atm of pressure at sea level, so the total pressure exerted on our diver is $28.8 \text{ atm} + 1 \text{ atm} = 29.8 \text{ atm}$. And since we are told that air is only 78% N_2 , then $p_{N_2} = (29.8 \text{ atm})(0.78 \text{ atm } N_2 / 1 \text{ atm}) = 23.2 \text{ atm}$. At the surface, we are told that 1.3 mL N_2 dissolves in 100 mL H_2O under 1 atm $N_2(g)$. By Henry's Law, $p_{N_2} = \kappa_{N_2} v_{N_2}$, so

$$\kappa_{N_2} = \frac{p_{N_2}}{v_{N_2}} = \frac{1 \text{ atm}}{\frac{1.3 \text{ mL}}{100 \text{ mL}}} = 76.9 \text{ atm}$$

Then, using this constant (the astute reader will notice that this is not the "canonical" Henry's law constant, but a slightly modified form, so I have called it κ instead of k),

$$v_{N_2} = \frac{p_{N_2}}{\kappa_{N_2}} = \frac{23.2 \text{ atm}}{76.9 \text{ atm}} = 0.302 = \frac{30.2 \text{ mL } N_2}{100 \text{ mL blood}}.$$

Thus, when returning to the surface, the amount of N_2 gas released is,

$$\left(\frac{30.2 \text{ mL } N_2}{100 \text{ mL blood}} - \frac{1.3 \text{ mL}}{100 \text{ mL}} \right) (2300 \text{ mL blood}) = 930 \text{ mL } N_2$$

If you think about the problem a bit, you'll realize that we have not included the compressibility of the water due to pressure $\kappa_T \approx 4.5$, nor the change in water temperature due to depth, both of which will change the density of the water, and hence the pressure as we calculated it. However, we have not learned how to account for either of these, so we will ignore their effects.

5.30a To solve this problem, we need only calculate $\Delta \bar{S}$ for each case (looking up the necessary thermodynamic values (I used the ones in Atkins, *Physical Chemistry*):

$$\begin{array}{lcl} H_2O(l, 0^\circ\text{C}) & \rightarrow & H_2O(l, 100^\circ\text{C}) \text{ Just heating, no phase change} \\ \Delta \bar{S} = \int \frac{dq_{rev}}{T} = \bar{C}_p \ln \frac{T_2}{T_1} = (75.291 \text{ J/mol K}) \ln \left(\frac{373 \text{ K}}{273 \text{ K}} \right) & = & 23.5 \text{ J/mol K} \end{array}$$

$$\begin{array}{lcl} H_2O(s, 0^\circ\text{C}) & \rightarrow & H_2O(l, 0^\circ\text{C}) \text{ Phase change only} \\ \Delta \bar{S} = \frac{\Delta H_{fusion}}{T} = \frac{6008 \text{ J/mol}}{273 \text{ K}} & = & 22.0 \text{ J/mol K} \end{array}$$

$$\begin{array}{lcl} H_2O(l, 100^\circ\text{C}) & \rightarrow & H_2O(g, 1 \text{ atm}, 100^\circ\text{C}) \text{ Phase change only} \\ \Delta \bar{S} = \bar{S}_g - \bar{S}_l = (188.83 \text{ J/mol K}) - (69.91 \text{ J/mol K}) & = & 118.92 \text{ J/mol K} \end{array}$$

$$\begin{array}{lcl} H_2O(g, 1 \text{ atm}, 100^\circ\text{C}) & \rightarrow & H_2O(g, 0.1 \text{ atm}, 100^\circ\text{C}) \text{ Pressure change} \\ \Delta \bar{S} = \int \frac{-dw_{rev}}{T} = \int \frac{p dV}{T} = - \int \frac{V dp}{T} = - \int \frac{nR dp}{p} \\ \Delta \bar{S} = -nR \ln \left(\frac{p_2}{p_1} \right) = -(8.315 \text{ J/mol K}) \ln \left(\frac{0.1 \text{ atm}}{1 \text{ atm}} \right) & = & 19.1 \text{ J/mol K} \end{array}$$

By comparing the calculated values, we see that the maximum entropy change occurs for the vaporization of water, i.e., $H_2O(l, 100^\circ\text{C}) \rightarrow H_2O(g, 1 \text{ atm}, 100^\circ\text{C})$.

5.30b Since we are considering the free energy of transfer of molecules from inside to outside, we can think of this as a reaction *inside* \rightarrow *outside*, with

$$\Delta G_{tr} = \Delta G^\circ + RT \ln \frac{a_{out}}{a_{in}}$$

Since equilibrium occurs when the osmotic pressures are equal, i.e, when the concentration inside and outside are the same, we know that $\Delta G^\circ = 0$. As a result, to find the greatest ΔG_{tr} , we need only find the greatest a_{out}/a_{in} ratio:

$$\frac{0.005}{0.100} < \frac{0.20}{0.10}, \frac{0.20}{0.10} < \frac{0.140}{0.010}$$

Therefore the largest value for ΔG_{tr} is for the $NaCl(a = 0.010 \text{ in}) \rightarrow NaCl(a = 0.140 \text{ out})$ case.